Temperature Dependence of Some Reactions of Singlet Oxygen with Olefins in the Gas Phase

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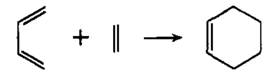
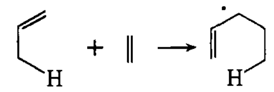
Abstract: Arrhenius parameters have been determined for the reactions of $O_2(^1\Delta_g)$ with some substituted butenes, cyclopentenes, and cyclohexenes. The preexponential factors were found to be fairly constant for this series ($A = 10^{8.1}$ to $10^{8.5}$ l. mol^{-1} sec^{-1}) while the activation energies, which varied from 3.2 to 7.5 kcal mol^{-1}, were found to be the source of the large differences in the room-temperature rate constants. The results are discussed in view of several transition states which have been proposed for this reaction.

The Diels-Alder reaction



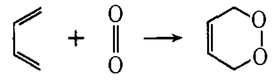
(1)

and the structurally related ene reaction



(2)

have been studied extensively and the results point to a single concerted, bimolecular, cyclic mechanism.[1,2] Singlet molecular oxygen ($O_2(^1\Delta_g)$) which lies 22.5 kcal above the triplet ground state possesses an electronic structure closely related to ethylene and, not unexpectedly, displays the same two types of reactions



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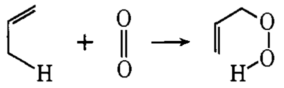


(4)

In view of this parallel, and the similar effect of substituents and solvents, most workers[3-5] have considered cyclic intermediates like those proposed for reactions 1 and 2 most acceptable for reactions 3 and 4, respectively. Though other intermediates have been proposed for the ene reaction of singlet oxygen,[6] there does not appear to be strong evidence for such alternative pathways.[7]

The present study was undertaken to obtain Arrhenius parameters for several ene reactions in the gas phase so that these could be compared with a few values already reported for the reaction in solution.[8] In our earlier studies of these reactions the rate constants were obtained by following the disappearance of singlet oxygen.[9] This yields the sum of the quenching and reaction rate and is susceptible to interference from other quenching species.[10,11] In this paper we report data obtained by following the rate of removal of the olefin.

Experimental Section

The apparatus used in these experiments is similar to that described by Huie and Herron.[11] It consisted of a conventional discharge-flow system in which the concentration could be followed mass spectrometrically. The inlet leak was drawn from a fine glass capillary, sealed into the downstream end of the flowtube and connected directly to the ionization chamber of and EA I-Quad 1210-A mass spectrometer. The reaction vessel was 1 m long, 4.9 cm in diameter, and made of Pyrex. It was surrounded with an electrically heated jacket which allowed the temperature to be maintained at any value between 300 and 500°K. Flowrates were typically 70 cm sec^{-1} or 1×10^{-4} mol sec^{-1} at a pressure of 2.5 Torr in the reaction tube.

A movable reactant inlet was used to establish the order of the reaction. However, the temperature dependence of k was determined with a fixed inlet 85 cm from the mass spectrometer inlet. The temperature was monitored with a copper-constantan thermocouple which was also placed on movable inlet to check the uniformity of the temperature along the reaction tube. The temperature was found to vary by less than 2° along the length of the tube.

Singlet oxygen was produced.in the conventional manner[9] using an electrodeless microwave discharge from which atomic oxygen was removed with a ring of mercuric oxide.[13] Final traces of atomic oxygen, which had previously been found to cause difficulties in such systems,[10] were removed by the addition of a small flow of nitrogen dioxide, shortly after the discharge region.

The $O_2(^1\Delta_g)$ concentration was measured at the midpoint of the reaction tube using an RCA 7265 photomultiplier. This monitored the 6340A emission band through a suitable interference filter and "honeycomb" collimating arrangement. The phototube signal was then amplified and displayed on a strip chart recorder. These readings were converted to absolute singlet oxygen concentrations by calibration against an isothermal calorimetric detector.[9] The calorimetric detector could not be used throughout the experiment because its cobalt surface became poisoned by the olefin at higher temperatures. Since the calibration was performed at a single reaction-tube temperature, readings at other temperatures had to be corrected for the temperature dependence of the dimol emission using the data of Arnold, Browne, and Ogryzlo.[14]

The addition of a relatively small amount of reactant allowed the rate of consumption of the olefin to be treated by pseudo-first-order kinetics since the $O_2(^1\Delta)$ concentration is not significantly affected. This leads to the following rate equation which was used to calculate the rate of constant "k".

$$\ln (S_0/S) = k[^1\Delta_g]t$$

Since the relative substrate concentration S/S_0 after a reaction time t was determined from the mass spectrometric peak heights in the presence and absence of a constant concentration of $O_2(^1\Delta_g)$ some care had to be taken to use a peak which displayed a negligible contribution from product molecules. In most cases a direct measurement of the mass spectrum of the product is difficult because of its low vapor pressure and instability. However, we have studied the alteration in the mass spectra as the reaction proceeds and observed that the parent peak of the olefin is one of several which show an identical and maximum percent decrease with increasing reaction time. This provides a very good indication that the product contributes negligibly to these peaks since it is unlikely that it would contribute equally to the whole set. In the case of 2,3-dimethylbutene-2, Herron and Huie[11] have shown more directly that the hydroperoxide product does indeed contribute negligibly to the parent peak of the olefin.

Olefins were obtained from Phillips Petroleum Co., in the highest purity available. However, the experimental technique employed in this work is particularly insensitive to impurities since individual reactants are observed directly with the mass spectrome-

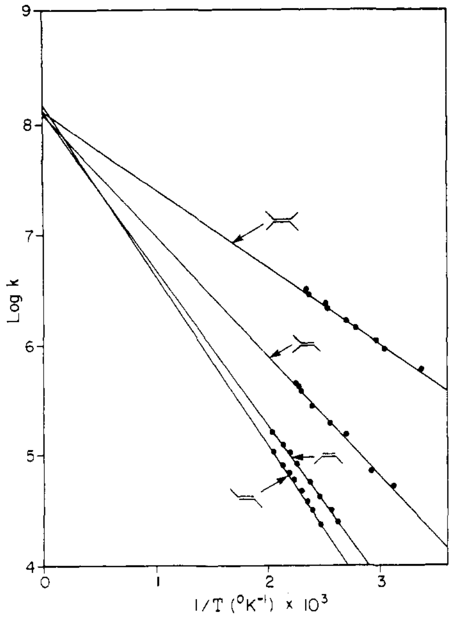


Figure 1. Arrhenius plot of the rate constants for the reaction of singlet oxygen with 2,3-dimethylbutene-2, 2-methybutene-2, *cis*-butene-2, and *trans*-butene-2 in the gas phase.

ter. The samples were degassed and used without further purification.

Results

Rate constants obtained in this investigation are presented in the Arrhenius plots shown in Figures 1, 2, and 3. Each point on the figures represents the average of several determinations of the rate constant obtained by varying the amount of added reactant. Arrhenius preexponential (A) factors and activation energies (E^*) were obtained from the intercepts and slopes of these lines. Table I lists these values, obtained by a least-squares analysis of the points. The errors quoted are 95% confidence limits of the point distribution. They tend to be somewhat greater for the less reactive molecules because of the narrower temperature range which was used for these compounds. The errors in the A factors are not independent of those on the activation energies but are related through the slope and mean point of each line.

Table I. Activation Energies and Preexponential Factors Obtained from the Data in Figures 1, 2, and 3

Compd	Log A	E^*, kcal/mol	Ionization energy, eV
2,3-Dimethylbutene-2	8.12 ± 0.09	3.23 ± 0.15	8.30
2-Methylbutene-2	8.10 ± 0.16	4.90 ± 0.28	8.60
cis-Butene-2	8.10 ± 0.14	6.47 ± 0.28	9.13
trans-Butene-2	8.20 ± 0.18	7.28 ± 0.36	9.13
1,2-Dimethylcyclobutene	8.44 ± 0.11	3.99 ± 0.18	
1-Methycyclohexene	8.38 ± 0.15	7.52 ± 0.30	
Cyclohexene	(8.4 assumed)	>8.2	8.72
1,2-Dimethylcyclopentene	8.50 ± 0.16	4.02 ± 0.28	
1-Methylcyclopentene	8.40 ± 0.16	5.98 ± 0.28	
Cyclopentene	8.35 ± 0.36	7.39 ± 0.71	9.1

Discussion

The temperature dependence of only one of these gas-phase reactions can be found in the literature. Hollenden and Timmons[15] have reported $E^* = 3.4$ kcal mol^{-1} and log $A = 8.83$ for the reaction of $O_2(^1\Delta_g)$ with 2,3-dimethylbutene-2. Both quantities are somewhat higher than those reported in Table I. Furthermore, their value for k (25°) is 1.8×10^6 l. mol^{-1} sec^{-1}. This is about three times the value which we obtain by a short extrapolation to 25° (6×10^5). There is good evidence that erroneously high values can be obtained in discharge-flow systems when care is not taken to eliminate oxygen atoms from the reaction vessel.[10,11] This may account for the discrepancy since NO_2 was not used by Hollinden and Timmons to ensure that this species was absent.

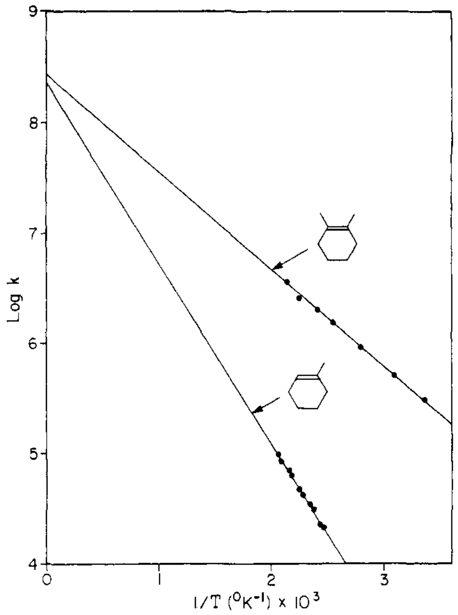


Figure 2. Arrhenius plot of the rate of constants for the reaction of singlet oxygen with 1,2-dimethylcyclohexene and 1-methylcyclohexene in the gas phase.

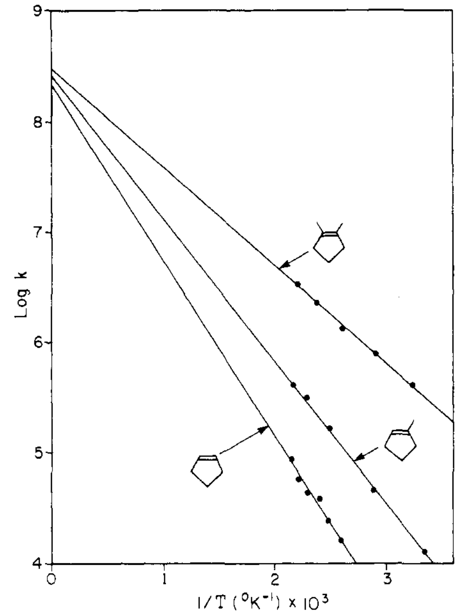
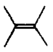
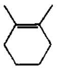
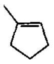


Figure 3. Arrhenius plot of the rate constants for the reaction of singlet oxygen with 1,2-dimethycyclopentene, 1-dimethycyclopentene, and cyclopentene in the gas phase.

A complete set of room-temperature rate constants obtained by extrapolation of the Arrhenius plots in Figures 1, 2, and 3 is listed in Table II. These values compare very favorably with some earlier values obtained by Herron and

Table II. Rate Constants and Arrhenius Parameters for Some Reactions $O_2(^1\Delta_g)$ in the Gas Phase and in Solution

	Gas phase			Solution		
Substrate	k(25°), l. mol^{-1} sec^{-1}	E^*, kcal/mol	Log A	k(25°), l. mol^{-1} sec^{-1}	E^*, kcal/mol	Log A
	6×10^5	3.2	8.1	2.4×10^7	0.5	7.7
	3×10^4	4.9	8.1	2.0×10^6	1.6	7.5
	2.3×10^3	6.5	8.1			
	9×10^2	7.3	8.2			
	3×10^5	4.0	8.4	1.3×10^7	1.3	8.00
	7.3×10^2	7.5	8.4	1.9×10^5		
	$<10^2$	>8.3	(8.4)	4.4×10^3	5.4	9.76
	3.2×10^5	4.0	8.5			
	1.2×10^4	6.0	8.4	1.7×10^6		
	9×10^2	7.4	8.4	7×10^4		

Huie,[11] under conditions where oxygen atoms were excluded. The values they obtained were

k(1, 2-dimethylcyclopentene) = 3.0×10 l. mol^{-1} sec^{-1}

k(1-methylcyclopentene) = 1.1×10 l. mol^{-1} sec^{-1}

k(2-methylbutene-2) = 3.3×10 l. mol^{-1} sec^{-1}

k(2, 3-dimethylbutene-2) = 7.7×10 l. mol^{-1} sec^{-1}

Koch[8] has determined rate constants and Arrhenius parameters for some of these reactions in methanol. The absolute values of these rate constants were based on a lifetime τ for $O_2(^1\Delta_g)$ which is incompatible with recent direct determinations of these quantities. We have therefore used an average of two such determinations of τ in methanol (9 μ sec[16,17]) together with new kinetic data obtained by Kopecky[18] and Foote[19] to calculate more accurate values of k (25°) and log A for these reactions in solution. Those available are all listed in Table II for comparison with the gas-phase data. Several interesting points arise from an inspection of these data.

(1) In the gas phase, *the large variation in reactivity of these olefins can be attributed almost entirely to differences in activation energy*, since the preexponential factor changes very little between reactants. Within experimental error, these changes in activation energy for both the linear olefins and cyclic pentenes can be reproduced if it is assumed that (a) the introduction of a methyl group reduces the activation energy by 1.5 kcal, (b) one group cis to another causes a further drop of 0.8 kcal, and (c) a second pair placed cis to one another causes an additional drop of 0.3 kcal. As many workers have pointed out,[3,6,7,8] this rate-accelerating effect of the methyl substituents is undoubtedly associated with the electron-donating ability of this group and the electrophillic nature of singlet oxygen. The lower activation energy for reaction with the cis isomer is consistent with the greater thermodynamic stability of the trans form, and this may be due to a slight distortion from a planar configuration in the cis isomer.

For the cyclohexene series the activation energies change much more rapidly with methyl substitution. Foote[4] has also noted this anomaly in the room-temperature rate constants for the reaction in solution, and has suggested that the differences are due to the difficulty in forming the endocyclic product. This is evident in the product distribution data collected in Table V. Arrhenius parameters for the formation of individual products in these reactions would be very useful in assessing the various possibilities.

(2) *The room-temperature rate constants in solution are about two orders of magnitude larger than those in the gas phase.* Since the preexponential factor is actually smaller in solution, the increased rate is entirely the consequence of a drop of about 3 kcal in the activation energy for most reactions.

Unfortunately few reactions have been studied in both the gas and condensed phase so that there remains some controversy over what differences should be expected. When either reactant is polar differences have been observed.[20] However, when both reactants are not very polar, it would appear that there is usually very little change in the Arrhenius parameters when the medium is altered. This is illustrated by the data for the dimerization of cyclopentadiene reproduced in Table III.[1]

Table III. Arrhenius Parameters for the Dimerization of Cyclopentadiene

Medium	Log A	E^*, kcal/mol
Gas phase	6.1	16.7
Benzene	6.1	16.4
Ethanol	6.4	16.4
CS_2	6.2	16.9

Such data are normally taken to indicate that the transition state in the reaction is not polar. In the present case, where the reactants are also "nonpolar," the difference between the two phases could be taken as evidence for a polar transition state. This appears to be in conflict with the often cited absence of a "solvent effect" for this reaction.[21] However, it is probably unwise to draw such a conclusion simply from the lack of variation of a rate constant with changes in solvent. It can be seen from the data in Table II that the effect of the solvent is to reduce both the activation energy (which raises k) and the preexponential factor (which lowers k). Such compensating effects are normal in these systems.[22] Consequently, when the activation energy becomes very small, as it does when these reactions are carried out in a solvent, the effect of any further change in E^* is decreased relative to the compensating change in A.

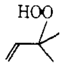
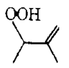
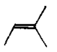
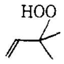
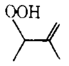
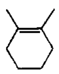
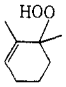
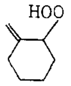
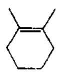
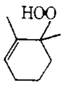
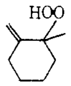
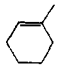
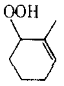
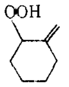
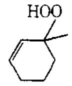
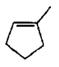
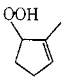
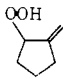
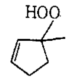
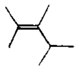
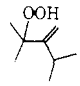
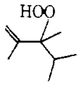
The most thorough study of solvent effects on these reactions of singlet oxygen was carried out by Foote and Denny.[21] Rate constants calculated from their values of β and recently determined lifetimes of singlet oxygen[16] are shown in Table IV together with some parameters which are considered a measure of the solvent polarity.[23] It can be seen that there is apparently a small solvent effect in the appropriate direction. However, in view of the low activation energy for this reaction (<2 kcal[8]) and the compensating

Table IV. Solvent Effects on the Singlet Oxygen Reaction with 2-Methyl-2-pentene

Solvent	k(25°),[a] l. mol^{-1} sec^{-1}	Dielectric constant	Z,[b] kcal/mol	$E_T(30)$[b]
Methanol	9×10^5	32.6	83.6	55.5
Acetone	5×10^5	20	65.7	42.2
Benzene	4×10^5	2.3	54	34.6
Carbon disulfide	2.5×10^5	2.64		32.6

[a] Values of k(25°) were calculated from the β values in ref 21 and lifetimes were given in ref 16. [b] See ref 23 for a discussion of these solvent parameters.

Table V

Reactant		Product (%)		Product (%)		Product (%)		Ref
	gas phase		(71)		(29)			32
	solution		(54)		(46)			3
	gas phase		(5)		(95)			32
	solution		(10)		(90)			3
	solution		(20)		(44)		(36)	33
	solution		(43)		(4)		(53)	32
	solution		(39)		(61)			

effects of changes in *A* under these conditions, the data are not inconsistent with the somewhat polar transition state postulated above. A good test of these suggestions would require a determination of the activation energy for the reaction in different solvents.

At least four different transition states have been proposed for this reaction.

(a) *A dioxetane intermediate* has been suggested by Fenical et al.[24] on the basis that stable dioxetanes can be isolated in some olefin reactions. However, all the available evidence points to the exclusive formation of carbonyl products from the decomposition of dioxetanes[25,28] and it therefore appears unlikely that they are intermediates in the reactions under consideration since these produce hydroperoxides exclusively.

(b) *The ene mechanism*[4] supposed a simple six-center cyclic intermediate analogous to that which is assumed in the conventional ene reaction. Though the lack of a strong solvent effect has been used by Foote[21] to argue against other more polar intermediates there is no reason to believe that the ene transition state would not be somewhat polar in view of the strong electrophillic nature of $O_2(^1\Delta_g)$. Consequently, the present data cannot be considered inconsistent with this mechanism.

(c) *The perepoxide intermediate* originally proposed by Sharp[26] was favored by some "azide trapping" experiments until it was discovered that the technique suffered from several complications and the results are inconclusive.[27] Since a perepoxide would be somewhat polar, this intermediate could account for the lower activation energy of these reactions in solution. Since the C–O bond in a perepoxide would be expected to break more easily at the electron-rich center, an anti-Markovnikoff addition would be anticipated with this intermediate. However, it can be seen from the data reproduced in Table V that for 2-methylbutene-2 in the gas phase there is in fact a positive Markovnikoff directing influence which favors oxygen bonding to the more electronegative center by a factor of 2.5. In the study of the deuterium isotope effect on the oxidation of 2,3-dimethylbutene-2, Kopecky and van de Sande[28] concluded that neither the perepoxides nor the 1,2-dioxetanes are involved in the singlet oxygen reaction. A more recent study of some cyclopentyl and cyclohexyl systems in the same laboratory reinforces this view.[34]

(d) *A charge-transfer complex* has been proposed for the analogous Diels–Alder reaction of singlet oxygen.[29] There is also some correlation between the ionization energies of the olefins and their reactivities (see Table I). It is important to observe, however, that if no bound species exists and there is simply a charge-transfer "interaction" in the transition state, the intermediate would be indistinguishable from that proposed in the ene mechanism. On the other hand a bound charge-transfer complex seems much less likely. Electronic relaxation of $O_2(^1\Delta_g)$ would probably be favored in such a complex unless the species were drawn together extremely strongly.[30] Since attempts to intercept[27] or isolate an intermediate at low temperatures[31] have been unsuccessful such a possibility has little to recommend it at the moment.

Conclusion

This study indicates that the reaction of singlet oxygen with olefins has a rather large and unvarying entropy of activation ($\Delta S_c \approx -23$ eu) and a small activation energy which is lowered by increasing methyl substitution at the double bond. A comparison with some data for the same reactions in solution suggests a somewhat polar transition state is involved. In the absence of any evidence for a bound intermediate this requirement can be accommodated by the simple "ene" mechanism.

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